No. 4.—A (63°, 17) followed by a (48°, 6) on the long track. The two images have their ends nearly super-imposed. Also a (140°, 16) lower down the photo. Note the short "spur" to this latter and compare it with the long spur due to the lighter "air" atom in No. 10.

No. 5.—A (31°, 26) followed by an (80°, 7).

No. 6.—One track showing an early bend (20°, 65) with a small spur.

No. 7.—A (42°, 19) bend also showing spur.

No. 8.—A (52°, 16) with a long spur. The left-hand image marked by an arrow shows that the three parts of the track are co-planar.

No. 9.—An early bend (39°, 18) with long spur. The unusual breadth of the r.-h. image is probably an optical effect.

No. 10.—A marked bend (132°, 18) indicating a nearly head-on collision. The r.-h. image is marked by an arrow.

No. 11.—A remarkable track showing an (895°, 59) bend. The direction of the initial part of the track upwards. The l.-h. image shows the remaining part of the track very much foreshortened. The long spur shows two marked bends, evidently due to collision of the recoil atom itself with two atoms of the gas. This track is the most suitable for accurate measurement, and for it the mass ratio m/M is found to be 3·3. Almost certainly then the atom collided with is a nitrogen atom.

On the Structure and Chemical Activity of Copper Films, and the Colour Changes accompanying their Oxidation.

By C. N. Hinshelwood, B.A., Fellow of Trinity College, Oxford.

(Communicated by Prof. J. W. Nicholson, F.R.S. Received August 30, 1922.)

When the surface of a metal is exposed to the action of a gas with which it reacts chemically, brilliant colour phenomena are frequently produced. In some cases the colours are recognised as diffraction colours, produced by the scattering of light in the surface film, and not as simple interference effects. When this is found the film must have a more or less complex structure, fine grained compared with the wave-length of light, but of a coarse-grained granular nature compared with molecular magnitudes. The work of Beilby has drawn attention from other points of view to the complex structure which the surface layers of metals, or thin films of metals, may assume.

It seems to be of considerable importance to correlate the chemical activity of such surface films with their structure, in view of the bearing this correlation may have on the problems of heterogeneous catalysis.

A first attempt in this direction is made in this paper, the reaction investigated being the oxidation and reduction of a copper—copper oxide film on the surface of metallic copper.

The general nature of the phenomena observed is as follows: When bright, rolled copper foil is exposed to the action of oxygen gas at low pressure, and at 200—300° C., a film of oxide forms on the surface, and, as oxidation proceeds, the velocity of oxygen absorption diminishes considerably, owing to the difficulty of penetration of the oxide film. The surface assumes various tints, all of which, however, are quite faint, finally becoming black. Its metallic lustre is retained throughout. After reduction, a second oxidation is brought about very much more readily than the first, and the surface assumes a new series of tints, brighter than the first, and even qualitatively distinct from them. Successive oxidations and reductions take place more and more readily until, ultimately, a limiting rate appears to be attained, which may be some hundreds of times greater than the original rate. As the surface becomes more and more active chemically the diffraction colours simultaneously increase in brilliancy. Ultimately a permanent colour sequence, with tints of great brilliancy, is established, which may be traversed time after time. The surface loses its metallic lustre, and when in the fully activated condition the copper is salmon-pink in colour.

During the activation process the structure of the surface film seems to change in the following way: At first the surface layers of the copper foil are compact as a result of its mechanical treatment; during the successive stages of activation by alternate oxidation and reduction, the copper atoms in the surface film are able, under the influence of surface tension, to aggregate themselves more and more completely into small discrete units in what Beilby calls "open formation," and the film assumes a granular structure freely permeable to oxygen. From the experiments to be described it is possible, in principle, to determine the size of these small granules, and although there are difficulties in the way of finding accurate values, it emerges clearly that the order of magnitude of their diameter is only a small fraction of 1μ. The view has been expressed that metallic grains as small as this assume a spherical form.* But Sir George Beilby has kindly pointed out to me that the evidence of microphotographs shows the film to be lenticular in structure. In the last section of this paper the magnitude of the granules is calculated, for the sake of simplicity, on the assumption that they are spherical. The radius thus determined will be their mean or "effective" radius.

Each small unit of copper will be oxidised independently, and the extent to which it is converted into oxide determines the colour of the diffracted light. The amounts of oxygen absorbed, corresponding to various well marked steps in the colour sequence, has been determined, and may, incidentally, be of interest in connection with the optics of the phenomenon.

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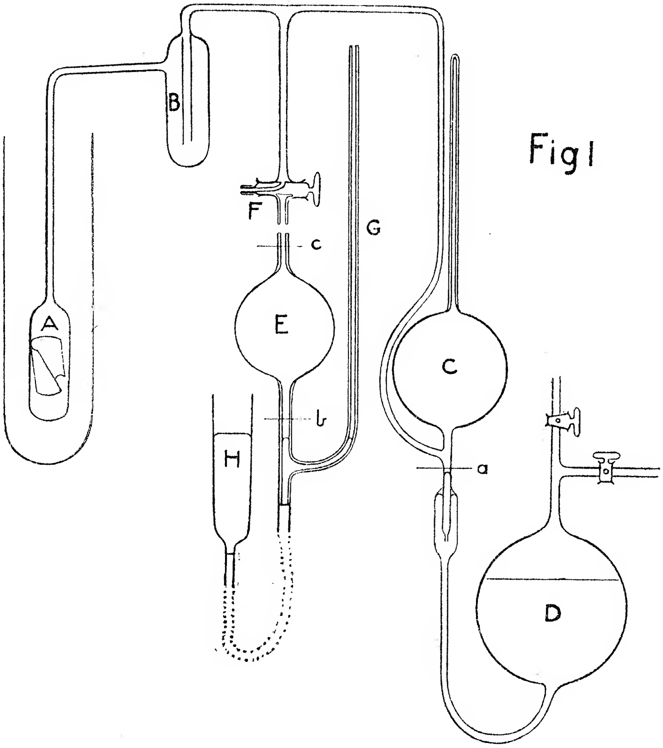
* Maxwell Garnett, 'Phil. Trans.,' A, vol. 205, p. 279.

There is a curious difference between the phenomena observed during reduction and those observed during oxidation, which suggests an interesting mechanism for the gradual activation of the film.

Experimental Method.

The amounts of oxygen, or hydrogen, absorbed were measured by means of a McLeod gauge, so constructed that it could be used over the range of pressures corresponding with the passage of the surface films through their various stages of colour. Pieces of copper foil, of known area, were used, and very carefully cleansed.

The apparatus is shown in fig. 1. Bulb A contains the copper, and is kept at constant temperature by being surrounded with the vapour of a liquid of suitable boiling point. CD is the McLeod gauge in a convenient form, similar to that described by Merton,* the mercury being raised, or lowered, by letting air into, or evacuating D, as required. B is a trap. E is a volumenometric device, connected to the main apparatus at the end of a series of experiments.



In an experiment the apparatus is evacuated by means of the three-way tap F, filled once or twice with oxygen, or hydrogen, and then evacuated to the desired pressure, which was initially about 1 mm. in one series of experiments and 4 mm. in another. To start an experiment the vapour jacket was placed round A, and the diminution of pressure with time was observed. Except when a reading is being made the mercury is kept at the mark *a*. To convert pressure readings to absolute measure the total volume of the apparatus needs to be known. The bulb A, moreover, and part of the connecting tube are at a high temperature, and the rest at room temperature. To find the effective volume of the whole, corrected for this temperature difference, connection is made to E, and air admitted at atmospheric pressure. The increase of pressure necessary to compress from *b* to *c* is measured on the gauge G, the mercury in the McLeod gauge always being kept at *a* by applying pressure to D. The volume between *b* and *c* being known, the effective volume of the rest at the actual temperature of E is readily found.

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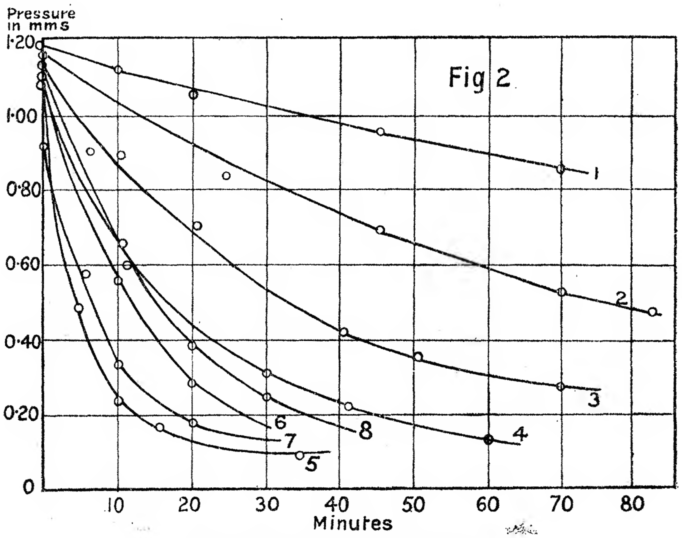
* 'Roy. Soc. Proc.,' A, vol. 90, p. 550.

With this apparatus it is possible to make measurements with considerable precision, as may be seen from fig. 2, in which the experimental points are marked on the curves.



Successive oxidations at 233°.

In the reduction experiments the minute amounts of water vapour present do not influence the readings, since the actual pressure in the capillary of the gauge when a reading is made is greater than the saturation pressure.

Retention of hydrogen by the reduced copper might have been expected to cause trouble. Only once in the course of about fifty experiments was there any indication of such a disturbing factor, and even then there was no proof that it arose definitely from this cause. Probably any minute amounts of hydrogen retained are oxidised even before the initial reading is taken.

Apart from their intrinsic interest it is necessary to observe the colour phenomena carefully, for the following reason. The colours being diffraction and not interference colours, depend upon the structure, and not upon the thickness of the film. That is to say, they are independent of the depth to which the granular active film extends and are determined solely by the size and degree of oxidation of the units constituting this film. Below the film is compact metal. The active film oxidises very rapidly indeed compared with the compact metal below, so that in an experiment not unduly prolonged we may regard the chemical changes as confined to this film. In order to give an absolute significance to a series of measurements of oxygen absorption, we must know the quantity of metal which composes the film taking part in the reaction. If we know the weights of oxygen necessary for the oxidation of two films to the same colour, we obtain the relative amounts of metal in the two; and if we know the weight of oxygen necessary to oxidise a given film black, that is completely to cupric oxide, then the amount of copper in the film is known. Quantitative results on the very large diminution in velocity of oxidation as soon as the black stage is reached leave little doubt that this does actually represent complete oxidation of the activated film, and that subsequent action depends upon the slow attack of the massive metal beneath.

The Colour Phenomena.

That the colours shown by oxidised copper and by tempered steel are due to diffraction was pointed out by Mallock,* who found that a film of given tint could be ground away while retaining its colour, which must therefore be dependent not upon its thickness, as it would be if interference were the cause, but upon its minute structure. Corroborative evidence is cited by Raman.† The relation to Beilby's observations has also been pointed out.

All the quantitative results of these experiments bear this out fully.

1. In the oxidation of copper, the brilliancy of the diffraction colours increases *pro rata* with the chemical activity, the granular film which most effectively scatters light presenting the largest surface to the action of the oxygen. When fresh copper is oxidised the colours are faint and the sequence is not constant, but is usually silvery or steely, pale straw, violet, black.

The permanent colour sequence is purple, blue, green, very light green (almost yellow), purple, blue, black. These are very brilliant, except the second appearance of purple and blue; they appear uniformly and are quite constant in hue from time to time.

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* 'Roy. Soc. Proc.,' A, vol. 94, p. 561.

† 'Nature,' January 26, 1922.

2. The absolute amount of oxygen absorbed corresponding to a given colour depends upon the amount of copper in the granular film, but the ratios of the amounts of oxygen required for the attainment of the various stages are constant. This shows clearly once more that the colours are structure colours. Thus for oxidation corresponding to maximum brightness, as far as the eye can judge, of the various colours, we have:—

	Grammes cupric oxide per 1 sq. cm. of foil.	Ratio taking light green as unity.	Grammes cupric oxide per 1 sq. cm. of same foil after heating for 10 hours in air and reduction.	Ratio.
Purple	0·000030	0·41	0·000067	0·38
Blue	0·000043	0·59	0·000115	0·64
Light green ...	0·000073	1·00	0·000178	1·00

The average of another series of experiments leads to the following set of ratios, taking the amount corresponding to light green as unity:—

Purple	0·40	Second purple..............	1·3
Blue	0·64	„ blue	1·6
Light green	1·00	Black	1·9

The oxidation of an active film must be imagined to consist in the independent oxidation of each of the small granules composing it, a layer of oxide being formed on the surface of each and extending inwards. The size and composition of each thus changes, and consequently the colour of the film alters. Thus, when the granules consist of approximately one-third oxide and two-thirds copper, the colour of the scattered light is bright blue. Within the boundary of each granular unit of copper or of copper oxide there is no reason to doubt that the density of the material is normal, the low mean density of the film being due to the spacing of the granules.

The effects observed during reduction differ in a remarkable manner from those observed during oxidation. No diffraction colours appear when a black film is reduced, the colour of the film at any stage of the reduction being simply a shade of brown, produced by the combination of the red colour of the copper and the black of the oxide.

At first it is natural to ask whether the difference can be due to the intermediate formation of cuprous oxide in one case and not in the other. But an intermediate stage of this kind should appear from the curves showing the relation between the amount of chemical change and time whereas no such indication is present. During reduction the copper is on the outside of the granules and the oxide on the inside, while during oxidation the positions are reversed. This might be the cause of the difference, the absence of diffraction colours during reduction being due to the great scattering powers of the metal, which enables a small particle thinly covered with copper to behave as though it were copper throughout.

A more probable explanation seems to be that, while in oxidation each existing spherule of copper is gradually converted into oxide, reduction necessitates the growth of fresh granules, which grow about nuclei of copper, so that the film does not consist of composite units, but is an assemblage of growing granules of copper and diminishing granules of oxide. The kinetics of the reduction lend some support to this suggestion, which is further strengthened by a rather curious phenomenon sometimes observed. If the film is not oxidised beyond about the green stage, then it may sometimes be made to re-traverse during reduction the same colour sequence as it passed through during oxidation, the considerable core of unoxidised copper in the granules being sufficient to maintain the original structure rather than allow the growth of fresh granules.

It should be mentioned that heating films of given colour in a vacuum over several hundred degrees produces no appreciable change in their colour.

Kinetics of the Oxidation and Reduction.

Experiments at high pressures have been made by Joannis,[*] Berger[†] and Stahl.[‡] Berger finds the velocity of oxidation to be nearly independent of the pressure of oxygen for pressures from 1000 to 100 mm., and only to fall off at pressures less than 100 mm.

In these experiments the pressures were low, and the velocity both of oxidation and reduction was dependent on the pressure.

Most attention was given to the gradual activation of the surface. Only typical results will be given in full, and the general nature of the others described.

Oxidation.—The formation of an active granular film is a gradual process requiring a number of oxidations and reductions. A limiting velocity appears ultimately to be reached, provided that the oxidations are confined to the film, and not prolonged so as to eat further into the massive metal below.

The equation connecting oxygen absorption with time is probably very complex, but since the main governing factor is the velocity of diffusion of oxygen through the oxide already formed, an approximate description of the process should be given by the equation

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[*] 'C. R.,' vol. 158, p. 1801 (1914).

[†] 'C. R.,' vol. 158, pp. 1502 and 1798 (1914).

[‡] 'J. S. C. I.,' vol. 33, p. 1158 (1914).

$$-dp/dt = \frac{kAp}{p_0 - p},$$

where A = total area of all the granules,
p = pressure of oxygen,
p_0 = initial pressure,

thus $p_0 - p$ is proportional to the amount of oxide already formed.

Hence $$kA = 1/t\{p_0 \log p_0/p - (p_0 - p)\}.$$

kA is found not to be really constant, though it should be pointed out that small differences in p make large changes in kA. Nevertheless, the variation in kA over a series of experiments due to the real change in A accompanying the change in structure of the film is large compared with the variations due to the imperfection of the formula. Hence kA serves as an approximate measure of the activity of the film.

1. Oxidation of Fresh Bright Foil (3·19 sq. cm.)
Temperature 302° C.
$p_0 = 4{\cdot}75$ mm.

t (minutes).	$p_0 - p$.	kA.
0	0	
30	0·32	
230	0·82	
510	1·56	$6{\cdot}4 \times 10^{-4}$
750	2·00	$8{\cdot}0 \times 10^{-4}$
1660	2·93	$9{\cdot}9 \times 10^{-4}$

2. Oxidation of Reduced Product of 1.
Temperature 302° C.
$p_0 = 5{\cdot}01$ mm.

t.	$p_0 - p$.	kA.
0	0	
20	1·38	110×10^{-4}
70	2·15	94×10^{-4}
110	2·31	72×10^{-4}

3. After four Oxidations and reductions.
Temperature 302° C.
$p_0 = 3{\cdot}80$ mm.

t.	$p_0 - p$.	kA.
0	0	
7	0·66	
13	1·24	200×10^{-4}
40	1·74	150×10^{-4}

4. Oxidation of Reduced Product of 3.
Temperature 302° C.
$p_0 = 4{\cdot}49$ mm.

t.	$p_0 - p$.	kA.
0	0	
5	0·83	180×10^{-4}
10	1·22	200×10^{-4}

5. Oxidation of Reduced Product of 4.
Temperature 302° C.
$p_0 = 3{\cdot}25$ mm.

t.	$p_0 - p$.	kA.
0	0	
4	0·28	
20	0·99	100×10^{-4}

In another series with different foil and at 233° C. the fresh foil gave the following kA values $4{\cdot}2 \times 10^{-5}$, 7·8, 8·3, $8{\cdot}4 \times 10^{-5}$, its area being 8·94 sq. cm. After a good surface film had been formed by heating in an electrically heated tube to about 360° and oxidising and reducing several times it gave a kA value of about 150×10^{-5}. Although the permanent colour sequence was established it was by no means fully activated for the lower temperature, and after five oxidations at 233°, in none of which the black stage was reached and which were all short enough to ensure that an inappreciable amount of the massive copper underneath had been attacked, $k\text{A}$ value of 4800×10^{-5} was reached. After this the activity decreased again.

The values for the experiment in which the greatest activity was exhibited may be quoted as typical:—

t. minutes.	p. obsd. (mm.).	p. calc. for $k\text{A} = 0{\cdot}048$.
0	1·23	1·23
2	0·97	0·93
5	0·62	0·61
10	0·39	0·43
15	0·30	0·33
75	0·12	0·08

Although it might have been expected that a film formed by repeated oxidation and reduction at a high temperature would show no further increase in activity in a series of experiments at a lower temperature, this appears not to be true. Fig. 2 illustrates a series made at 233° with a film formed by over forty oxidations and reductions at 400°. During formation oxidation was carried to the black stage each time, during the experiments only to the purple stage.

The curves are numbered in the order in which the experiments were performed. Here, again, the activity reaches a limit and declines slightly. The maximum activity corresponded with a $k\text{A}$ value of about 7000×10^{-5}. The limiting rate would naturally be reached when the granular film had attained a condition of maximum stability where it was incapable of further sub-division, but the possibility of loss of activity by poisoning with traces of impurity in the oxygen or hydrogen must not be lost sight of.

Reduction.—Joannis at 100–600 mm. found that the reduction was not retarded by the copper formed to the same extent as the oxidation was retarded by the oxide. Berger found an induction period in the reduction of the oxide. This could not have been due to the necessity for water-vapour to be produced since water-vapour actually retards the reduction.

Both of these observations are confirmed by the low-pressure experiments, but it was found that there was no induction period at first. As the series proceeded and the foil grew more active both with respect to oxidation and reduction an induction period made its appearance.

These observations all fit in with the suggestion that reduction does not proceed through the original granules of oxide, but that fresh nuclei of copper grow at the expense of the oxide nuclei. Any change which depends upon nucleus formation may show an induction period, and often is accelerated in an autocatalytic manner. There are evident signs of such acceleration in the curves showing the progress of the reduction with time.

The growth of fresh granules of copper during reduction offers a simple picture of how the activation by alternate oxidation and reduction comes about.

Order of Magnitude of the Granules Composing the Film.—On the simple assumption already made we have

$$\mathrm{A} = \frac{1}{kt}\{p_0 \, ln \, p_0/p-(p_0-p)\}. \tag{1}$$

If the film consist of n granules of radius r then

$$4\pi r^2 n = \mathrm{A}, \tag{2}$$

also m, the mass of oxide in the oxidised film, will be given by

$$4/3\pi r^3 n \times 5{\cdot}9 = m, \tag{3}$$

assuming the normal density (5·9) of the oxide within the limits of the granule.

These determine r if k is known. This is the main difficulty. We will first find some values of r/k. As in most cases the films were not oxidised to the black stage, the amount of oxygen corresponding to light green was used for the calculation of m with the aid of the ratios given in the section on the colours. Three experiments at 233° lead to values of

r/k of 4×10^{-2}, 2×10^{-2}, and $1{\cdot}5 \times 10^{-2}$.

At 302° with different copper with films more or less in the state of maximum activity 27×10^{-2} and 29×10^{-2} were found.

To find k we must obtain the value of kA in an instance where A is known. The simplest way is to assume that with new foil when the metal is still in the compact form the measured area of the foil is also that governing diffusion. On this basis a value of k of the order 10^{-5} was found for the 233° series, which leads to a value for the diameter of the granules of the order 0·005 μ. In the series at 302° the value of k arrived at on the same assumption was of the order 3×10^{-4} which leads to a value for the diameter of about 0·17 μ. Owing to the crudeness of the assumption which must be made in finding k these figures only show the order of magnitude, but would appear to represent major limits, since the foil, even in the compact state, almost certainly offers to the attack of the oxygen an area considerably greater than its apparent area. We cannot, therefore, attach importance to the difference in the values found at 233° and 302°, but both sets of values show the degree of dispersion of the metal in the film to be very great. The particles are small enough therefore to assume forms in which the influence of surface tension predominates.

I hope to improve the method of investigation by employing films of the attackable metals deposited on an inert metal.

On Measurements of Electrode Potential Drop with Direct Current and Alternating Current Electrolysis.

By S. Marsh, B.Sc., Ph.D., and A. E. Evans, B.Sc.

(Communicated by E. H. Griffiths, F.R.S. Received April 29, 1922.)

§1.

The investigations to be described in this paper are the outcome of some work by one of the authors on alternating current electrolysis,* in which the behaviour of platinum, gold and nickel electrodes, using dilute sulphuric acid and barium hydrate solution as electrolytes, was examined for alternating current with frequencies lying between 25 cycles and 80 cycles per second. Some provisional measurements of the electrode drop were made at that time, but it was felt desirable to examine this feature in greater detail.

The apparatus employed for the purpose is shown in fig. 1. The electrolyte was contained in a glass tube EF, 60 cm. long and 4 cm. diameter, provided with a feed tube D. The ends were closed with rubber stoppers, each pierced with two holes, through which passed tubes holding electrodes A and C and an "explorer" B, and a thermometer T. The electrode C was of platinum, and remained unchanged throughout all the experiments.

A was the experimental electrode, rectangular in shape, area approximately 0·4 sq. cm. Electrodes of double and half this area were also employed to investigate the effect of current density.

It was attached to a short platinum wire which was sealed through the tube, and electrical contact was made by mercury with wires from the supply. The "explorer" B consisted of a fine platinum wire (0·05 mm. diameter) which projected about 1 or 2 mm. from a fine glass tube sealed

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* S. Marsh, 'Roy. Soc. Proc.,' A, vol. 97, pp. 124–144.